

Superconductivity in La_3Pt_4

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We found superconductivity of intermetallic La_3Pt_4 below 0.51 K, while searching for the Pt-substituted material of the noncentrosymmetric (NCS) superconductor LaNiC_2 ($T_c = 2.7 \text{ K}^{1,2}$).

Superconductors with NCS crystal structures, which do not have spatial inversion symmetry, have been attracting much attention since the discovery of the absence of the Pauli limiting field in CePt_3Si .³ Recently, some interesting superconducting properties were reported in LaNiC_2 .¹ This compound crystallizes in the CeNiC_2 -type orthorhombic structure (space group $\text{Amm}2$), which lacks the inversion symmetry along the c -axis (see Fig. 1). A recent muon spin relaxation (μSR) result suggests unconventional superconductivity.⁴ On the other hand, first-principle calculations for this material suggested that it is likely to be a conventional superconductor judging from its s -orbital-dominant electronic states near the Fermi energy.⁵ Further confirmation of unconventional properties is needed for this material.

In NCS superconductors, antisymmetric spin-orbit interaction (ASOI) due to the absence of spatial inversion symmetry may lead to a spin singlet-triplet mixed superconducting state. A number of unconventional superconducting properties are predicted, but most of them are yet to be observed.⁶ Since stronger ASOI is considered essential for the emergence of the unconventional superconducting properties, it is desirable to investigate NCS superconductivity in compounds containing heavy elements. For LaNiC_2 , replacements of Ni with heavier elements such as Pd or Pt seem favorable to realize large ASOI.

We tried to synthesize LaMC_2 ($M = \text{Ni, Pd, Pt}$) samples using the arc melting method. The starting materials were La (purity 99.9%), Ni (99.999%), C (99.999%), Pd (99.95%), and Pt (99.98%). These materials were melted in argon with the stoichiometric ratio of $\text{La}:M:\text{C} = 1:1:2$. Powder X-Ray diffraction (XRD) measurements (Bruker AXS, D8 ADVANCE) were

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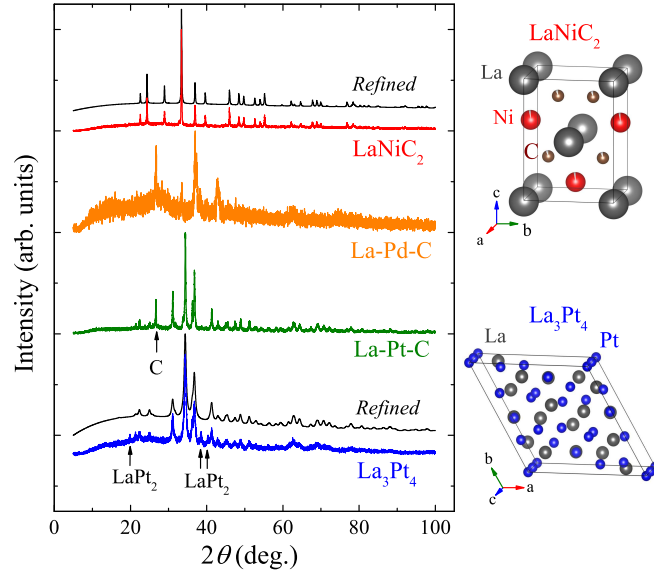


Fig. 1. (Color online) Powder XRD patterns of LaNiC_2 , La-Pd-C , La-Pt-C , and La_3Pt_4 samples (Cu $K\alpha$ radiation). The two patterns in black show the refined XRD patterns obtained by the Rietveld method. The impurity peaks of carbon (in La-Pt-C) and LaPt_2 (in the La_3Pt_4 sample) are indicated. The right figures show the crystal structures of LaNiC_2 and La_3Pt_4 . These schematics are drawn using the software VESTA.¹⁰

carried out (Fig. 1). As represented in Fig. 1, the samples for $M = \text{Ni}$ are almost single-phase LaNiC_2 . The XRD patterns of La-Pd-C and La-Pt-C samples do not resemble that of LaNiC_2 . Further XRD analysis revealed that carbon remains unreacted in La-Pt-C samples, and that its main constituent is actually La_3Pt_4 , not “ LaPtC_2 ”. La_3Pt_4 crystallizes in the rhombohedral Pu_3Pd_4 -type structure (space group $R\bar{3}$,⁷ see Fig. 1). Note that its crystal structure has inversion symmetry.

New samples were synthesized by arc melting from stoichiometric mixture of $\text{La}:\text{Pt} = 3:4$ for La_3Pt_4 . As presented in Fig. 1, the XRD pattern of a La_3Pt_4 sample well agrees with that of La-Pt-C . The XRD indicates that its main phase is certainly La_3Pt_4 although it contains a small amount ($<20\%$) of LaPt_2 ($T_c = 0.46 \text{ K}$ ⁸) impurity. Except for LaPt_2 , no impurity phases are detected in this sample. The lattice parameters of La_3Pt_4 obtained using the Rietveld analysis were $a = 13.8 \text{ \AA}$, $c = 5.83 \text{ \AA}$, which agree with the literature.⁷

The AC susceptibility χ_{AC} of the synthesized La-Pt-C sample and La_3Pt_4 is presented in Fig. 2. The measurements were performed by a mutual-inductance technique with a home-built first-derivative coil, mounted in a commercial ^3He refrigerator (Oxford Instruments, Heliox). For La_3Pt_4 , strong magnetic shielding indicating bulk superconductivity is observed below 0.51 K . Similar shielding signal is also observed in the La-Pt-C sample, indicating

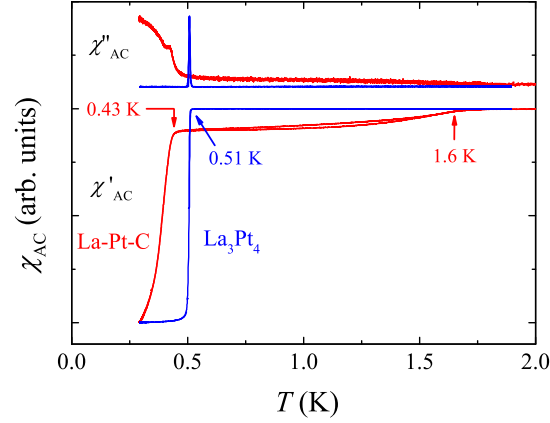


Fig. 2. (Color online) Temperature dependence of the real and imaginary parts of the AC magnetic susceptibility χ_{AC} of the samples of La-Pt-C and La_3Pt_4 down to 0.3 K. The AC magnetic field H_{AC} was 1 μT -rms, and its frequency was 887 Hz for the La-Pt-C sample and 3011 Hz for the La_3Pt_4 sample.

that La_3Pt_4 is indeed the majority phase in this sample. In addition, weak magnetic shielding below 1.6 K is observed only in the La-Pt-C sample. The shielding is presumably a superconducting impurity phase, but the origin is unclear. Note that LaC_2 is known to exhibit superconductivity below 1.6 K,⁹ although the corresponding XRD peaks are not detected.

The resistivity of La_3Pt_4 under 0 T and 0.1 T is presented in Fig. 3(a). It was measured by a conventional DC four-probe technique with Heliox as well. The zero-resistivity temperature 0.5 K well agrees with the onset temperature of χ_{AC} . The residual resistivity ratio $RRR \equiv \rho_{300\text{K}}/\rho_{1\text{K}}$ is approximately 30 (not shown) for the present polycrystalline samples. The specific heat c_p divided by temperature in several magnetic fields is presented in Fig. 3(b). The heat capacity was measured using a relaxation-time-method with a commercial apparatus (Quantum Design, PPMS) down to 0.35 K. The molar specific heat are evaluated assuming single-phase La_3Pt_4 . The clear and large specific heat jump at 0.5 K in 0 T due to the transition indicates the bulk superconductivity.

Superconductivity is suppressed by a magnetic field of 0.1 T, as evidenced by both ρ and c_p/T measurements. The normal state c_p/T is independent of the applied magnetic field within the experimental resolution. Thus c_p/T at 0.1 T can be used to evaluate specific-heat coefficients: c_p/T in the normal state is fitted by the relation $c_p/T = \gamma + \beta T^2$, where γ and β are the electronic and the phononic specific-heat coefficients, respectively. The value of γ is evaluated to be 15.5 mJ/(f.u.mol·K²). We also calculated γ based on the first-principle calculation using the WIEN2k package¹³ as 3.0 mJ/(f.u.mol·K²). Thus, the electronic mass

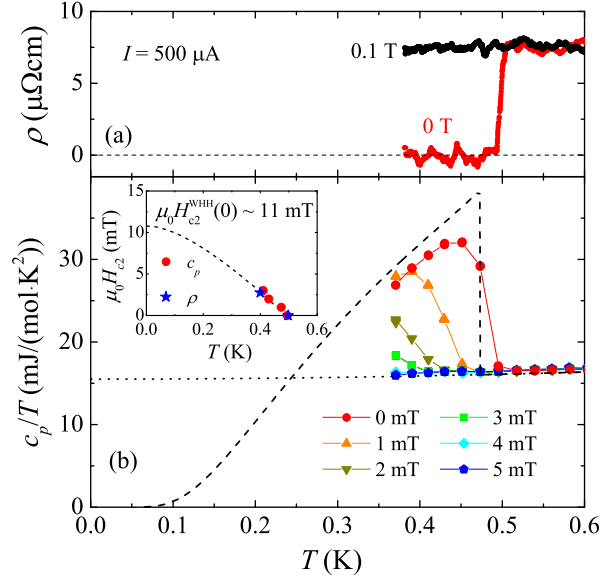


Fig. 3. (Color online) (a) Temperature dependence of ρ of La_3Pt_4 under 0 T and 0.1 T at low temperatures. (b) Temperature dependence of c_p/T of La_3Pt_4 at low temperatures. The dotted line is a fit of $c_p/T = \gamma + \beta T^2$ to the normal state data up to 2.0 K. The obtained parameters are $\gamma = 15.5$ mJ/(f.u.mol·K²) and $\beta = 2.40$ mJ/(f.u.mol·K⁴). The curve based on the conventional BCS theory deduced from γ and $T_c = 0.47$ K is also presented.¹¹ The inset shows the upper critical field $H_{c2}(T)$ determined from the onset T_c of c_p/T (red circles) and the resistive midpoint (blue stars). The dashed line is the WHH curve for $H_{c2}(T)$ in the dirty limit,¹² giving $\mu_0 H_{c2}^{\text{WHH}}(0) = -0.693T_c[d(\mu_0 H_{c2})/dT]|_{T=T_c} = 11$ mT.

enhancement is approximately 5. The obtained β value is 2.4 mJ/(f.u.mol·K⁴), yielding the Debye temperature $\Theta_D = 178$ K from the relation $\beta = (12/5)\pi^4 N_A N_{\text{f.u.}} k_B / \Theta_D^3$. Here N_A is the Avogadro number, $N_{\text{f.u.}} = 7$ is the number of atoms per formula unit, and k_B is the Boltzmann constant.

The specific-heat jump height Δc_p divided by γT_c is smaller than that of the weak-coupling BCS theory: 1.43. The fact suggests existence of residual density of states that does not contribute to the superconductivity. The residual density of states is attributable to impurity phases that were detected in the X-ray spectrum in Fig. 1. Improvement of sample quality as well as measurements down to a lower-temperature region is necessary for further investigation.

The superconducting $H - T$ phase diagram based on the onset T_c of c_p/T and the resistive midpoint is presented in the inset of Fig. 3(b). The conventional Werthamer-Helfand-Hohenberg (WHH) curve¹² with the onset $T_c = 0.5$ K and the initial slope

$[d(\mu_0 H_{c2})/dT]|_{T=T_c} = 32 \text{ mT/K}$ is also shown. The WHH upper critical field is estimated to be 11 mT. From this value, we crudely estimate the zero-temperature GL coherence length $\xi(0)$ as 170 nm, using the orbital depairing relation $\mu_0 H_{c2}^{\text{WHH}}(0) = \Phi_0/[2\pi\xi^2(0)]$.

In summary, we found that centrosymmetric La_3Pt_4 exhibits superconductivity below 0.51 K, while trying to synthesize LaPdC_2 and LaPtC_2 using arc melting.

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References

- 1) W. Lee, H. Zeng, Y. Yao, and Y. Chen: *Physica C* **266** (1996) 138 .
- 2) V. K. Pecharsky, L. L. Miller, and K. A. Gschneidner: *Phys. Rev. B* **58** (1998) 497.
- 3) E. Bauer, G. Hilscher, H. Michor, C. Paul, E. W. Scheidt, A. Griбанov, Y. Seropegin, H. Noël, M. Sigrist, and P. Rogl: *Phys. Rev. Lett.* **92** (2004) 027003.
- 4) A. D. Hillier, J. Quintanilla, and R. Cywinski: *Phys. Rev. Lett.* **102** (2009) 117007.
- 5) A. Subedi and D. J. Singh: *Phys. Rev. B* **80** (2009) 092506.
- 6) S. Fujimoto: *J. Phys. Soc. Jpn.* **76** (2007) 051008.
- 7) A. Palenzona: *J. Less-Common Met.* **53** (1977) 133 .
- 8) T. H. Geballe, B. T. Matthias, V. B. Compton, E. Corenzwit, G. W. Hull, Jr., and L. D. Longinotti: *Phys. Rev.* **137** (1965) A119.
- 9) R. W. Green, E. O. Thorland, J. Croat, and S. Legvold: *J. Appl. Phys.* **40** (1969) 3161.
- 10) K. Momma and F. Izumi: *J. Appl. Crystallogr.* **44** (2011) 1272.
- 11) B. Mühlischlegel: *Z. Phys.* **155** (1959) 313.
- 12) N. R. Werthamer, E. Helfand, and P. C. Hohenberg: *Phys. Rev.* **147** (1966) 295.
- 13) K. Schwarz and P. Blaha: *Comput. Mater. Sci.* **28** (2003) 259.